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(54) **Non-iridescent glass structures and processes for their production**

(57) This invention relates to transparent glass windows 20 of the type bearing a first coating 26 of infra-red reflective material, which is advantageously less than about 0.85 microns in thickness wherein the observance of iridenscence resulting from such a first coating is markedly reduced by the provision of a second coating 24 arranged in register with said first coating, the second coating providing at least two interfaces which, with the mass of the second coating, form means to reflect-and-refract-light therefrom to interfere with the observation of iridescence. The invention also relates to processes for producing such windows. A particular advantage of the invention is its efficacy with clear and lightly tinted glasses wherein the problem of iridescent colour has had its greatest commercial impact.
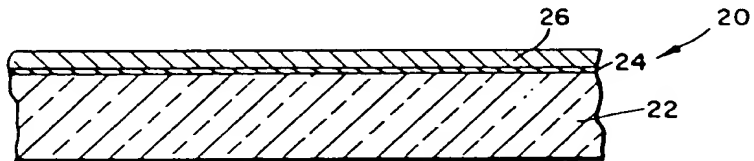
FIG. 2

R — red
B — blue
G — green
Y — yellow

SnO$_2$ ON GLASS

SnO$_2$ AND SINGLE LAYER UNDERCOAT ON GLASS

SnO$_2$ AND DOUBLE LAYER UNDERCOAT ON GLASS

OBSERVABILITY THRESHOLD
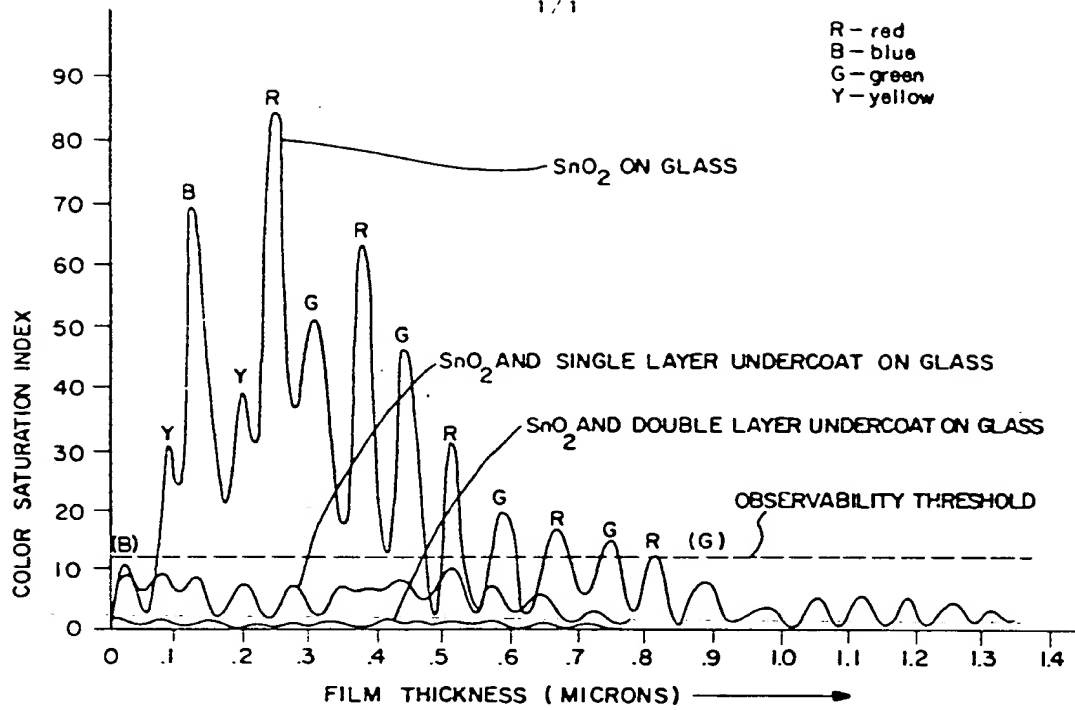
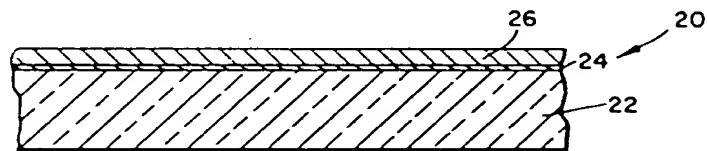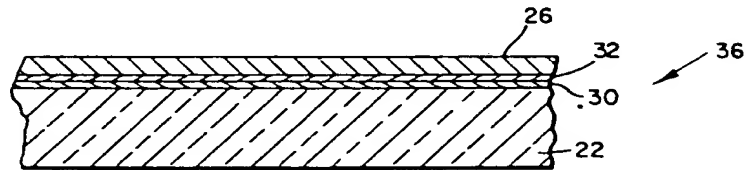COLOR SATURATION INDEX

FILM THICKNESS (MICRONS)

FIG. I

FIG. 2

FIG. 3
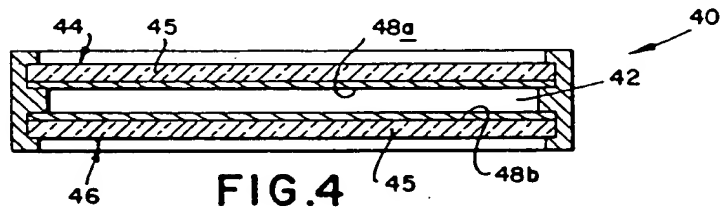
FIG. 4

SPECIFICATION

Non-iridescent glass structures and processes for their production

5 This invention relates to glass structures bearing a thin, functional, inorganic coating (e.g. a   5
coating of tin oxide forming means to promote reflectivity of infra-red light) which structures
have improved appearance as a consequence of reduced iridescence historically associated with
said thin coatings, and methods for achieving the aforesaid structures.
    Glass and other transparent materials can be coated with transparent semiconductor films
10 such as tin oxide, indium oxide or cadmium stannate, in order to reflect infra-red radiation. Such   10
materials are useful in providing windows with enhanced insulating value (lower heat transport)
in ovens, architectural windows, etc. Coatings of these same materials also conduct electricity,
and are employed as resistance heaters to heat windows in vehicles in order to remove fog or
ice.
15   One objectionable feature of these coated windows is that they show interference colors   15
(iridescence) in reflected light, and, to a lesser extent, in transmitted light. This iridescence has
been a serious barrier to widespread use of these coated windows (see, for example, American
Institute of Physics Conference Proceeding No 25, New York, 1975, Page 288.
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Institute of Physics Conference Proceeding No 25, New York, 1975, Page 288.)
    In some circumstances, i.e. when the glass is quite dark in tone (say, having a light
transmittance of less than about 25%) this iridescence is muted and can be tolerated. However,
35 in most architectural wall and window applications, the iridescent effect normally associated with   35
coatings of less than about 0.75 microns is aesthetically unacceptable to many people (See, for
example, U.S. Patent 3,710,074 to Stewart). Little or no success has been achieved in
substantially reducing or eliminating the objectionable and apparent iridescence in clear, blue-
green and lightly tinted glasses.
40   Iridescent colors are quite a general phenomenon in transparent films in the thickness range   40
of about 0.1 to 1 micron, especially at thicknesses below about 0.85 microns. Unfortunately it
is precisely this range of thickness which is of practical importance in most commercial
applications. Semiconductor coatings thinner than about 0.1 micron do not show interference
colors, but such thin coatings have a markedly inferior reflectance of infra-red light, and a
45 markedly reduced capacity to conduct electricity.   45
    Coatings thicker than about 1 micron also do not show visible iridescence, in daylight
illumination, but such thick coatings are much more expensive to make, since larger amounts of
coatings materials are required, and the time necessary to deposit the coating is correspondingly
longer. Furthermore, films thicker than 1 micron have a tendency to show haze, which arises
50 from light scattering from surface irregularities, which are larger on a such film. Also, such films   50
show a greater tendency to crack, under thermal stress, because of differential thermal
expansion.
    As a result of these technical and economic constraints, almost all present commercial
production of such coated glass articles comprise films in the thickness range of about 0.1 to
55 0.3 microns, which display pronounced iridescent colors. Almost no architectural use of this   55
coated glass is made at present, despite the fact that it would be cost-effective in conserving
energy to do so. For example, heat loss by infra-red radiation through the glass areas of a
heated building can approximate about one-half of the heat loss through uncoated windows. The
presence of iridescent colors on these coated glass products is a major reason for the failure to
60 employ these coatings.   60
    It is one object of the present invention to provide means to eliminate the visible iridescence
from semiconducting thin film coatings on glass, while maintaining their desirable properties of
visible transparency, infra-red reflectivity, and electrical conductivity.
    Another object of the present invention is to achieve the above goals without increasing the
65 cost of production significant over the cost of using ordinary iridescent films.   65

Another object of the present invention is to achieve the above aims with a process which is
continuous and fully compatible with modern manufacturing processes in the glass industry.

A further object of the present invention is to achieve all of the above goals with products
which are highly durable and stable to light, chemicals and mechanical abrasion.

5 Another object is to achieve all of the above goals using materials which are sufficiently   5
abundant and readily available to permit widespread use.

Still another object of the invention is to provide a novel double-glazed structure bearing an
ultra-thin, infra-red-reflective substance, which structure is free of objectionable iridescence.

Another object of the invention is to provide a glass structure comprising a compound coating
10 wherein an outer coating is formed of an infra-red reflecting surface of about 0.7 microns or less   10
and wherein an inner coating forms means for (a) reducing haze on the coated glass and,
simultaneously and independently (b) reducing the iridescence of the glass structure by means
of coherent addition of reflected light.

A further object of the invention is to provide a glass structure having the non-iridescent
15 characteristics referred to above which structure is characterized by a step-wise, or a graduated,   15
change in coating composition between glass and air.

Other objects of the invention will be obvious to those skilled in the art on reading the instant
invention.

One aspect of the invention utilizes the formation of one or more layers of transparent material
20 between the glass and the semiconductor film. These layers have refractive indices intermediate   20
between those of the glass and the semi-conductor film. With suitable choices of thickness and
refractive index values, it has been discovered, the iridescent colors can be made too faint for
most human observers to detect, and certainly too faint to interefere with widespread
commercial use even in architectural applications. Suitable materials for these intermediate
25 layers are also disclosed herein, as well as processes for the formation of these layers.   25

Another novel method disclosed and claimed herein is the assembling of two glass surfaces
with coatings offset from one another by 0.25 of a visible wavelength in thickness (e.g. about
0.07 microns when tin oxide coatings are used) in register with one another such that light
which would form the iridescent colors is incoherently added, effectively reducing any
30 undesirable iridescent effect below the threshold of aesthetic objection.   30

Examples of this invention include a double glazed windows with one coating on each sheet
or a single sheet of glass with a coating on each glass surface.

A unifying aspect of these various embodiments is that they all utilize a thin semiconductor
coating arranged congruently with a second coating which forms means to substantially
35 diminish iridescence by providing at least two additional interfaces forming means, with the   35
mass of the second coating, to reflect and refract light in such a way that it markedly interferes
with the observation of any iridescent colors.

It is believed desirable, because of the subjective nature of color perception, to provide a
discussion of the methods and assumptions which have been used to evaluate the inventions
40 disclosed herein. It should be realized that the application of much of the theory discussed   40
below is retrospective in nature because the information necessarily is being provided in
hindsight, i.e. by one having a knowledge of the invention disclosed herein.

In order to make a suitable quantitative evaluation of various possible constructions which
suppress iridescent colors, the intensities of such colors were calculated using optical data and
45 color perception data. In this discussion, film layers are assumed to be planar, with uniform   45
thickness and uniform refractive index within each layer. The refractive index changes are taken
to be abrupt at the planar interfaces between adjacent film layers. Real refractive indices are
used, corresponding to negligible absorption losses within the layers. The reflection coefficients
are evaluated for normally incident plane waves of unpolarized light.

50 Using the above assumptions, the amplitudes for reflection and transmission from each   50
interface are calculated from Fresnel's formulae. Then these amplitudes are summed, taking into
account the phase differences produced by propagation through the relevant layers. These
results have been found to be equivalent to the Airy formulae (see, for example, *Optics of Thin
Films*, by F. Knittl, Wiley and Sons, New York, 1976) for multiple reflection and interference in
55 thin films, when those formulae applied to the same cases we considered.   55

The calculated intensity of reflected light has been observed to vary with wavelength, and
thus is enhanced in certain colors more than in others. To calculate the reflected color seen by
an observer, it is desirable first to specify the spectral distribution of the incident light. For this
purpose, one may use the International Commission on Illumination Standard Illuminant C,
60 which approximates normal daylight illumination. The spectral distribution of the reflected light   60
is the product of the calculated reflection coefficient and the spectrum of Illuminant C. The color
hue and color saturation as seen in reflection by a human observer, are then calculated from this
reflected spectrum, using the uniform color scales such as those known to the art. One useful
scale is that disclosed by Hunter in Food Technology, Vol. 21, pages 100–105, 1967. This
65 scale has been used in deriving the relationship now to be disclosed.   65

The results of calculations. for each combination of refractive indices and thicknesses of the
layers. are a pair of numbers. i.e. "a" and "b". "a" represents red (if positive) or green (if
negative) color hue. while "b" describes a yellow (if positive) or blue (if negative) hue. These
color-hue results are useful in checking the calculations against the observable colors of samples
5   including those of the invention. A single number. "c". represents the "color saturation":   5
$c = (a^2 + b^2)^{1/2}$. This color saturation index. "c". is directly related to the ability of the eye to
detect the troublesome iridescent color hues. When the saturation index is below a certain value.
one is not able to see any color in the reflected light. The numerical value of this threshold
saturation for observability depends on the particular uniform color scale used. and on the
10   viewing conditions and level of illumination (see. for example. R. S. Hunter. *The Measurement*   10
of Appearance. Wiley and Sons. New York. 1975. for a recent review of numerical color scales).
In order to establish a basis for comparison of structures a first series of calculations was
carried out to simulate a single semiconductor layer on glass. The refractive index of the
semiconductor layer was taken at 2.0. which is a value approximating tin oxide. indium oxide.
15   or cadmium stannate films. The value 1.52 was used for the glass substrate; this is a value   15
typical of commercial window glass. The calculated color saturation values are plotted in Fig. 1
as a function of the semi-conductor film thickness. The color saturation is found to be high for
reflections from films in the thickness range 0.1 to 0.5 microns. For films thicker than 0.5
microns. the color saturation decreases with increasing thickness. These results are in accord
20   with qualitative observations of actual films. The pronounced oscillations are due to the varying   20
sensitivity of the eye to different spectral wavelengths. Each of the peaks corresponds to a
particular color. as marked on the curve (R = red. Y = yellow. G = green. B = blue).
Using these results. the minimum observable value of color saturation was established by the
following experiment: Tin oxide films with continuously varying thickness. up to about 1.5
25   microns. were deposited on glass plates. by the oxidation of tetramethyltin vapor. The thickness   25
profile was established by a temperature variation from about 450°C to 500°C across the glass
surface. The thickness profile was then measured by observing the interference fringes under
monochromatic light. When observed under diffuse daylight. the films showed interference
colors at the correct positions shown in Fig. 1. The portions of the films with thicknesses greater
30   than 0.85 micron showed no observable interference colors in diffuse daylight. The green peak   30
calculated to lie at a thickness of 0.88 micron could not be seen. Therefore. the threshold of
observability is above 8 of these color units. Likewise. the calculated blue peak of 0.03 μ could
not be seen. so the threshold is above 11 color units. the calculated value for this peak.
However. a faint red peak at 0.81 μ could be seen under good viewing conditions. e.g. using a
35   black velvet background and no colored objects in the field of view being reflected. so the   35
threshold is below the 13 color units calculated for this color. We conclude from these studies
that the threshold for observation of reflected color is between 11 and 13 color units on this
scale. and therefore we have adopted a value of 12 units to represent the threshold for
observability of reflected color under daylight viewing conditions. In other words. a color
40   saturation of more than 12 units appears as a visibly colored iridescence. while a color '   40
saturation of less than 12 units is seen as a neutral.
It is believed that there will be little objection to commercialization of products having color
saturation values of 13 or below. However. it is much preferred that the value be 12 or below
and. as will appear in more detail hereinafter. there appears to be no practical reason why the
45   most advantageous products according to the invention. e.g. those characterized by wholly   45
color-free surfaces. i.e. below about 8. cannot be made economically.
A value of 12 or less is indicative of a reflection which does not distort the color of a reflected
image in an observable way. This threshold value of 12 units is taken to be a quantitative
standard with which one can evaluate the success or failure of various multilayer designs. in
50   suppressing the iridescence colors.   50
Coatings with a thickness of 0.85 micron or greater have color saturation values less than this
threshold of 12. as may be seen in Fig. 1. Experiments reported in example 15 confirm that
these thicker coatings do not show objectionable iridescence colors in daylight illumination.
One embodiment of the invention involves using a single undercoat to avoid reflected color
55   saturation. This requires use of a carefully selected single layer of a refractive-index (n_i) which is   55
intermediate between the refractive index of the glass (n_{gl} or about 1.52) and the refractive
index of the semiconductor (n_{sc} or about 2.0). An intermediate refractive index which is the
geometric mean $n_i = (n_{sc}n_{gl})^{1/2}$ or about 1.744. will result in the reflections from the two surfaces
of the intermediate layer having the same amplitude. By choosing the thickness of the
60   intermediate layer to be 1/4 wavelength. these two reflected waves cancel each other. and do   60
not contribute to the iridescent colors. This cancellation is exact at only a single wavelength
value. and the wavelength must be carefully selected. Therefore. an investigation was carried
out to find those values which reduced the color saturation index for semiconductor films.
particularly in the thickness range 0.15 to 0.4 μ. which semiconductors are of most interest for
65   heat reflection and have been a particular problem with respect to iridescence. The optimum   65

intermediate film thickness for an undercoat (i.e. a coat intermediate between glass and
semiconductor) was found to be about 0.072μ (72 nanometers), which corresponds to 1/4
wavelength for a (vacuum) wavelength of 500 nanometers. The color saturation remains *below*
the threshold value of 12 units, for semiconductor films of all thicknesses, as may be seen from
5   the curve in Fig. 1 Thus, the usual strong iridescence colors from a heat-reflecting film of, say,   5
0.3μ thickness, can be suppressed even by this single intermediate film undercoat.
      The sensitivity of this single layer, anti-iridescent undercoat to variations in refractive index
and thickness was studied. Changes of $\pm .02$ in refractive index or $\pm 10\%$ in thickness are
sufficient to raise the color saturation to observable values. Accurate control of these parameters
10   can be achieved in known glass coating operations. For example, U.S. Patent 3,850,679   10
describes an apparatus capable of coating to $\pm 2\%$ thickness uniformity.
      An effective product also can be formed using two layers of intermediate refractive indices on
the glass under the semiconductor film. For semiconductor films in the thickness range of 0.1 to
0.4μ, it was found to be possible to provide color saturation of only about one (1) unit or less!
15   This range is very much below the threshold for observability. For example, the two intermediate   15
refractive (n_1 and n_2) indices for such a construction are given by
      $n_1 = (n_g)^{.26}(n_s)^{.74}$ or about 1.63
      $n_2 = (n_g)^{.74}(n_s)^{.26}$ or about 1.86
      The optimum thicknesses are about 1/4 wavelength for (vacuum) wavelength 500 nanomet-
20   ers or about   20
      $d_1 = 76.7$ nm
      $d_2 = 67.2$ nm
      The layer of lower refractive index (n_1) is next to the glass, while the higher index (n_2) is next
to the semiconductor film.
25   This double undercoat design is even more tolerant of deviations of its parameters from the   25
optimum values, than is the single undercoat design. Variations of $\pm 25\%$ away from the
optimum thickness still suppress the iridescence values below the observable limit, i.e. below a
color saturation value of 10. Thus, very effective designs can be based on refractive-indices-in-
the ranges
30   $n_1 = (n_g)^{.26 = .03}(n_s)^{.74 = .03}$ 30
      $n_2 = (n_g)^{.74 = .03}(n_s)^{.26 = .03}$
which corresponds to a range of n_1 from 1.62 to 1.65, and a range of n_2 from 1.88 to 1.84.
The degree of manufacturing accuracy required to maintain coating thickness to a tolerance of
$\pm 25\%$, is readily achieved with state-of-the art procedures. Likewise, the accuracy needed for
35   the refractive indices is entirely practicable even when mixed materials are needed to obtain the   35
required values.
      It has also been discovered that a film intermediate between the glass substrate and a
semiconductor layer can be build up of a graded composition, e.g. gradually changing from a
silica film to a tin oxide film. Such a film is best pictured as one comprising a very large number
40   of intermediate layers.   40
      A wide range of transparent materials are among those which can be selected to make
products meeting the aforesaid criteria by forming anti-iridescent undercoat layer or layers.
Various metal oxides and nitrides, and their mixtures have the correct optical properties of
transparency and refractive index. Table A lists some mixtures which have the correct refractive
45   index for a single layer coating between glass and a tin oxide or indium oxide film. The weight   45
percents necessary are taken from measured refractive index vs. composition curves, or are
calculated from the usual Lorentz-Lorenz law for refractive indices of mixtures (Z. Knittl, *Optics
of Thin Films*, Wiley and Sons, New York, 1976, page 473), using measured refractive indices
for the pure films. This mixing law generally gives sufficiently accurate interpolations for optical
50   work, although the calculated refractive indices are sometimes slightly lower than the measured   50
values. Film refractive indices also vary somewhat with deposition method and conditions
employed.
      A routine pre-production check can be made easily, and, if necessary, one can adjust the
compositions to optimum values if such performance is really required.
55   Aluminum oxide films, for example, show some variability in refractive index, from about 1.64   55
to 1.75, depending on deposition conditions. In Tables A, B and C, Al_2O_3–h designates the
high-index (n = 1.75) films, while Al_2O_3–l designates the low index (n + 1.64) films. Films of
intermediate index of refraction require intermediate compositions to produce the desired
refractive indices
60   Tables B and C list some mixtures which have the correct refractive index (of about 1.63 and   60
1.86, respectively) for use in a double interlayer between glass substrate and a primary
semiconductor coating.
      In addition to these optical properties, suitable undercoat layers are selected to be chemically
durable and resistant to air, moisture, cleaning solutions, etc. Such a requirement eliminates, for
65   most purposes, germanium dioxide films of the type which are subject to easy water hydrolysis.   65

Films formed of about half GeO_2 and half SnO_2 do appear to be insoluble and resistant to attack by water.

TABLE A
Dielectric Films with Refractive Indices of Approximately 1.73–1.77

Mixtures	Component A	Weight %	Component B	Weight %
1	Si_3N_4	67 ± 4	SiO_2	33 ± 4
2	Al_2O_3–h	100	—	
3	ZnO	78 ± 3	SiO_2	22 ± 3
4	Al_2O_3–l	55 ± 8	ZnO	45 ± 8
5	MgO	76 ± 11	ZnO	24 ± 11
6	SnO_2	81 ± 3	SiO_2	19 ± 3
7	SnO_2	50 ± 7	Al_2O_3–l	50 ± 7
8	MgO	73 ± 11	SnO_2	27 ± 11
9	In_2O_3	81 ± 3	SiO_2	19 ± 3
10	In_2O_3	50 ± 7	Al_2O_3–l	50 ± 7
11	MgO	73 ± 12	In_2O_3	27 ± 12
12	GeO_2	55 ± 7	ZnO	45 ± 7
13	GeO_2	52 ± 7	SnO_2	48 ± 7
14	GeO_2	51 ± 7	In_2O_3	49 ± 7
15	Ga_2O_3	91 ± 3	SiO_2	9 ± 3
16	Ga_2O_3	71 ± 10	Al_2O_3–l	29 ± 10
17	MgO	53 ± 20	Ga_2O_3	47 ± 20
18	Ga_2O_3	70 ± 10	GeO_2	30 ± 10

TABLE B
Dielectric Films with Reflective Indices of Approximately 1.62–1.65

Mixture	Component A	Weight %	Compoment B (balance)
1	SiO_2	53 ± 4	Si_3N_4
2	Al_2O_3–l	100	—
3	Al_2O_3–l	97 ± 3	SiO_2
4	Al_2O_3–h	74 ± 5	SiO_2
5	ZnO	59 ± 4	SiO_2
6	MgO	79 ± 5	SiO_2
7	SnO_2	62 ± 3	SiO_2
8	In_2O_3	63 ± 3	SiO_2
9	GeO_2	100	—
10	Ga_2O_3	71 ± 3	SiO_2

TABLE C
Dielectric Films which have Refractive Indices of Approximately
$1.36 \pm .02$

Mixture	Component A	Weight %	Component B (balance)
1	Si_3N_4	84 ± 3	SiO_2
2	ZnO	91 ± 2	SiO_2
3	ZnO	76 ± 5	Al_2O_3-l
4	ZnO	59 ± 9	Al_2O_3-h
5	ZnO	68 ± 7	MgO
6	SnO_2	91 ± 2	SiO_2
7	SnO_2	78 ± 5	Al_2O_3-l
8	SnO_2	60 ± 8	Al_2O_3-h
9	SnO_2	70 ± 6	MgO
10	In_2O_3	91 ± 2	SiO_2
11	In_2O_3	78 ± 5	Al_2O_3-l
12	In_2O_3	61 ± 8	Al_2O_3-h
13	In_2O_3	71 ± 6	MgO
14	ZnO	75 ± 7	GeO_2
15	SnO_2	76 ± 7	GeO_2
16	In_2O_3	76 ± 4	GeO_2
17	Ga_2O_3	80 ± 14	ZnO
18	Ga_2O_3	79 ± 14	SnO_2
19	Ga_2O_3	78 ± 15	In_2O_3

Note—Al_2O_3-h = high-density aluminum oxide film n of about 1.7
Al_2O_3-l = low density aluminum oxide film n of about 1.6

All of these films can be formed by simultaneous vacuum evaporation of the appropriate materials of an appropriate mixture. For coating of large areas, such as window glass, chemical vapor deposition (CVD) at normal atmospheric pressure is more convenient and less expensive. However, the CVD method requires suitable volatile compounds for forming each material. The most convenient sources for CVD are gases at room temperature. Silicon and germanium can be deposited by CVD from gases such as silane, SiH_4, dimethylsilane $(CH_3)_2SiH_2$, and germane (GeH_4). Liquids which are sufficiently volatile at room temperature are almost as convenient as gases; tetramethyltin is such a source for CVD of tin compounds, while $(C_2H_5)_2SiH_2$ and $SiCl_4$ are volatile liquid sources for silicon. Similarly, trimethyl aluminum and dimethyl zinc, and their higher alkyl homologs, furnish volatile sources for these metals. Less convenient, but still useful, sources for CVD are solids or liquids which are volatile at some temperature above room temperature but still below the temperature at which they react to deposit films. Examples of this latter category are the acetylacetonates of aluminum, gallium, indium and zinc (also called 2, 4 pentanedionates), aluminum alkoxides such as aluminum isopropoxide and aluminum ethylate, and zinc propionate. For magnesium, no convenient compounds are known which are volatile below deposition temperature, so CVD processes are not believed to be applicable to the preparation of magnesium oxide films.

Typical conditions under which metal oxide films have been successfully formed by chemical vapor deposition are summarized in Table D. Typically, the organometallic vapor is present in about one percent (by volume) in air. The films thus formed show good adhesion to both the glass substrate, and to subsequently deposited layers of tin oxide or indium oxide. Mixed oxide layers have been formed between all these pairs of metals, using CVD techniques (except for magnesium, for which a conveniently volatile compound was not available). The refractive indices of the mixed films are measured conveniently by taking the visible reflection spectra as a function of wavelength. The positions and heights of the maxima and minima in the reflected intensity can then be related to the refractive index of the deposited film. The concentrations of the reagent species are then adjusted to form the desired refractive index.

Using these methods, a number of samples have been made on borosilicate glass (Pyrex, Registered Trade Mark), using $(SiO_2 - Si_3N_4)$, $(SiO_2 - SnO_2)$, $(GeO_2 - SnO_2)$, $(Al_2O_3 - SnO_2)$, $(Al_2O_3 - Ga_2O_3)$, or $(Al_2O_3 - ZnO)$ mixed layers under a 0.3μ thick SnO_2 semiconductor layer. When the refractive index and thickness are correctly adjusted, the reflected daylight is neutral and colorless to the eye. The coatings are clear and transparent, and free of visible haze (scattered light).

TABLE D
Some Volatile Oxidizable Organometallic Compounds Suitable for Depositing Metal Oxide
Layers. and Mixed Metal Oxide Layers with Oxidizing Gases Such as O_2 or N_2O

	Compound	Volatilization Temperature (°C)	Deposition Temperature (°C)
1	SiH_4	gas at 20	300–500
2	$(CH_3)_2SiH_2$	gas at 20	400–600
3	$(C_2H_5)_2SiH_2$	20	400–600
4	GeH_4	gas at 20	300–450
5	$(CH_3)_3Al$	20	400–650
6	$Al(OC_2H_5)_3$	200–300	400–650
7	$Al(OC_3H_7)_3$	200–220	400–600
8	$Al(C_5H_7O_2)_3$	200–220	500–650
9	$Ga(C_5H_7O_2)_3$	200–220	350–650
10	$In(C_5H_7O_2)_3$	200–220	300–600
11	$(CH_3)_2Zn$	20	100–600
12	$Zn(C_3H_5O_2)_2$	200–250	450–650
13	$(CH_3)_4Sn$	20	450–650
14	$Ta(OC_4H_9)_5$	150–250	400–600
15	$Ti(OC_3H_7)_4$	100–150	400–600
16	$Zr(OC_4H_9)_4$	200–250	400–600
17	$Hf(OC_4H_9)_4$	200–250	400–600

When these same depositions were tried on ordinary window glass ("soda-line" or "soft"
glass) many of the resulting coatings showed considerable haze or scattered light. When the
layer first deposited on soft glass is amorphous and consists of SiO_2, Si_3N_4 or GeO_2 or mixtures
thereof. the coating is free of haze. no matter what the subsequent layers are. Al_2O_3 also gives
clear coatings, provided it is deposited in the amorphous form, advantageously below a
temperature of about 550°C. If the initial layer contains large proportions of Ga_2O_3. ZnO. In_2O_3.
or SnO_2. then haze formation is likely.

The first anti-iridescence layer to be deposited on a window glass surface is advantageously
amorphous. rather than crystalline, in structure. Silicon oxy-nitride is preferred. Subsequently
deposited layers can be of a polycrystalline form, without causing any haze.

Sodium and other alkali ions exert a deleterious effect on the infra-red reflectivity and
electrical conductivity of tin oxide and indium oxide films.

The aforesaid amorphous films and especially silicon oxynitride films are good barriers to the
diffusion of sodium ions from the glass into the semiconductor layer. By changing the
oxygen/nitrogen ratio in the films, the entire range of refractive index from that of glass with a
refractive index of about 1.5 to that of tin oxide or indium oxide with refractive indices of about
2. can be covered. Thus with the same basic reagents. anti-iridescence structures with any
number of refractive index steps can be fabricated. Indeed. even films with continually changing
proportion of reactants can be prepared. Only abundant and inexpensive materials are needed to
form silicon oxynitride.

Numerous volatile reagents are available to form silicon oxynitride films. Table E lists some of
the more convenient volatile materials for chemical vapor deposition of silicon oxynitride. The
reaction $SiH_4 + NO + N_2H_4$ is preferred. because it appears to give higher deposition rates in the
temperature range of interest for window glass. i.e. 500°C to 600°C. However. numerous other
combinations of reagents can also give successful silicon oxynitride films.

TABLE E
Source Materials for Chemical Vapor Deposition of Silicon Oxynitride Films

5 Sources of Silicon
    SiH_4
    $(CH_3)_2SiH_2$
    $(C_2H_5)_2SiH_2$
    $(CH_3)_4Si$
10 $SiCl_4$
    $SiBr_4$
   Sources of oxygen:
    O_2
    H_2O
15 N_2O
   Sources of nitrogen:
    N_2H_4 CH_3NHNH_2
    NH_3 $(CH_3)_2NNH_2$
    HN_3
20 Sources of both oxygen and nitrogen:
    NO
    NH_2OH
    $N_2H_4H_2O$

25   Interference colors, i.e. the iridescence, may be reduced by use of reflections from *two* thin coatings of a functional inorganic coating on separate, but parallel, glass surfaces. When coating thicknesses, e.g. thicknesses of tin oxide coatings, are selected to differ by about 1/4 of a wavelength (about .07 micron for $\lambda = 0.50\ \mu m$ and $n + 2.0$), the interference coloration practically disappears. Certainly it is reduced to the point where it ceases to become an aesthetic problem for supplier and customer. The additive coloration of, say, a red reflection in one coating and a green reflection of an adjacent interference order in a second coating, combine to produce a practically white (neutral) reflection. Similarly, the transmission of light through such a combination of complementary coatings is also neutral in color.
    This color compensation is used in double glazing to reduce the strength of the interference
35 colors from the heat-reflecting semiconductor coatings. For example, if coatings of SnO_2 are used on the two inner surfaces of a double glazed window, they can be chosen to differ in thickness by .07 μ. For extended light sources, the reflection colors are well cancelled if the glass surfaces are reasonably parallel. For small light sources, or ones with sharp boundaries, the compensation in reflection will not be complete unless the coating surfaces are highly
40 parallel. For observations in transmission, the requirements for parallel surfaces are not nearly as severe.
    It should also be noted that films in which the interference colors have been reduced in intensity by an undercoat of intermediate or graded refractive index, can also be combined in pairs to produce still further color compensation.
45   In order that the present invention may be more readily understood, reference will now be made to the accompanying drawings, in which:—
    Figure 1 is a graph illustrating the variation of calculated color intensity of various colors with semiconductor film thickness.
    Figure 2 illustrates, schematically and in section, a non-iridescent coated glass constructed
50 according to the invention, with a single anti-iridescent interlayer.
    Figure 3 illustrates, schematically, and in section, a non-iridescent coated glass, constructed according to the invention, with plural anti-iridescent interlayers.
    Figure 4 illustrates, schematically and in section, a double glazed window structure which exhibits a substantially improved appearance as a result of coatings carried thereof which reduce
55 or eliminate objectionable iridescence.
    Referring to Fig. 2, it is seen that transparent sheet 20 comprises a glass substrate 22, carrying an intermediate film 24 of 0.072 microns of Si_3N_4/SiO_2 (or of any of the other materials in Table A) having an index of refraction of 1.744. Over film 24 is a coating 26 of 0.4 microns of an infra-red reflecting semiconductor, tin oxide.
60   Fig. 3 illustrates a window 36 constructed of the same semi-conductor film 26 and the same glass 22 and two intermediate coatings as follows: Coating 30 which is 0.077 microns thick and has a refractive index of about 1.63. Coating 32 is about 0.067 microns and has a refractive index of about 1.86. Coating 30 is formed of any of the materials disclosed in Table B. Coating 32 is formed of any of the materials disclosed in Table C.
65   Fig. 4 illustrates a double-glazed window structure 40, enclosing an insulating air space 42

between an inner transparent sheet 44 and an outer transparent sheet 46. Each of sheets 44 and 46 are formed of glass 45 and a semiconductor coating 48a or 48b on the inner surface of the glass.

The semiconductor coating 48a is of about 0.2 microns thick, but coating 48b is about 0.27
5 microns thick; thus, there is a difference of about 1/4 wavelength in the two coatings.

Example 1

A glass with a single anti-iridescent undercoat layer, was produced by heating a clear window glass disc. 6 inches diameter, to about 580°C. A gas mixture containing about 0.4% silane
10 (SiH_4). 0.1% nitric oxide (N O), 2% hydrazine N_2H_4), and balance nitrogen (N_2) was passed over the glass surface for about one minute, at a rate of 1 liter/minute. This coated the glass surface with a uniform, transparent film of silicon oxynitride. The surface was then further coated with a fluorine-doped tin oxide layer, by flowing a gas mixture of 1% tetramethyltin $(CH_3)_4Sn$, 3% bromotrifluoromethane CF_3Br, 20% oxygen O_2, balance nitrogen N_2, past the silicon oxynitride
15 surface at 560°C for about one minute. Then the coated glass was allowed to cool slowly in air to room temperature, over a period of about one hour.

The glass coated by this procedure did not show visible interference colors in reflected or transmitted daylight. The surface reflected about 90% of infrared radiation at a 10 micron wavelength, and transmitted about 90% of visible light. The electrical sheet resistance was
20 measured to be about 3 ohms/square.

In order to measure the properties of the silicon oxynitride layer, the tin oxide film was removed from an area of the coated surface by rubbing with a mixture of zinc dust and diluted hydrochloric acid. This etchant does not affect the silicon oxynitride undercoat. The refractive index of the silicon oxynitride film was measured to be 1.74 by the CH_2I_2 liquid test described
25 below. The visible reflectivity of the silicon oxynitride film was measured, finding a maximum at 5000Å and a thickness of 0.072 micron, corresponding to the desired 1/4 wavelength thickness for 5000Å light.

The refractive indices of these silicon oxynitride films depend on the nitrogen-to-oxygen ratio in the films. This composition is easily adjusted by varying the N_2H_4/NO ratio in the gas.
30 Increasing the N/O ratio increases the refractive index. The exact refractive index also depends on the purity of the starting materials, and particularly on the amount of water present as an impurity in the hydrazine. Commercial hydrazine always contains at least a few percent water. By drying the hydrazine through distillation from a drying agent, such as sodium hydroxide, potassium hydroxide, or barium oxide, one can increase the refractive index of the film.
35 Conversely, one can decrease the refractive index by adding water to the hydrazine. The film refractive index also depends on the exact conditions of film growth, including deposition temperature, gas flow rate, etc. Therefore the conditions disclosed above cannot be expected to give a film of precisely n + 1.74, when other reagents or deposition conditions are used. However, small adjustments of the composition should be sufficient to produce films of the
40 desired refractive index values.

The semiconductor films may also have refractive indices different from the value 2.0 observed for the tin oxide films described herein. The corresponding optimum value(s) for a single (or double) undercoat layer(s) may then be adjusted, by the relationships given above. The corresponding gas-phase compositions which produce the desired refractive index films for
45 anti-iridescent undercoat(s) may then be found by routine experimentation, to fit the precise conditions of any manufacturer or investigator having ordinary skill in the CVD art.

The thickness of a film of measured refractive index is easily determined by measuring its reflection spectrum in visible and infra-red light. This spectrum is readily calculated, as a function of film thickness, using the standard optical formulas of Fresnel and Airy. In most of
50 the practical designs disclosed above, one desires to form a film of 1/4 wavelength thickness, for a wavelength (in air) of about 5000Å. In this case the reflection spectrum of a single such film on glass, shows a broad maximum centered at a wavelength of 5000Å.

Example 2
55 Aluminum 2,4 pentanedionate, $Al(C_5H_7O_2)_3$, (also known as aluminum acetylacetonate) is a white solid which melts at 189°C to a clear liquid, which boils at 315°C. This material was placed in a bubbler heated to about 250°C, through which nitrogen carrier gas was passed. When this gas mixture was mixed with dry oxygen at 250°C, no reaction was noted. However, when moisture was added to the oxygen, intense white fumes formed in the gas mixture. Such
60 fumes are indicative of hydrolysis. In order to prevent this premature hydrolysis reaction, the gas streams must be kept as dry as possible.

The mixture of aluminum 2,4 pentanedionate vapor, nitrogen carrier gas and 20% oxygen was passed over heated glass surfaces. At 500°C, a faint deposit was formed, less than 0.1 μ thick, which was evident only by its increased reflectivity. At 525°C a film 0.3 μ thick was
65 grown in about 3 minutes. This film showed faint interference colors under white light, and

distinct interference bands under monochromatic illumination. At 550°C the aluminum oxide
films grew even faster and a small amount of powder formed by homogeneous nucleation, and
deposited on the apparatus surface.

Next, fluorine-doped tin oxide films were grown on top of the aluminum oxide films at
5   temperatures in the range of 500°C to 540°C. Thickness in the range of 0.3 to 0.5 μ were   5
examined carefully, for these thicknesses show the strongest interference colors. The intensity of
the colors were substantially reduced, when compared to tin oxide films of the same thickness,
without the aluminum oxide undercoat.

Films in which the aluminum oxide film has 1/4 wavelength thickness (500 nm wavelength,
10 which is near the peak of the spectral sensitivity of the eye for daylight illumination) exhibit the   10
greatest suppression of iridescent color. For these thicknesses (approximately .072 μ for 1/4
wavelength, the reflections from the glass-Al_2O_3 and Al_2O_3-SnO_2 interfaces cancel each other
most effectively. However, there is also some substantial reduction in color intensity, even when
the thickness of the Al_2O_3 is not optimum.
15 As glass substrates, both Pyrex borosilicate glass, and soda lime (window) glass were used.   15
Good results were obtained on both substrates.

The aluminum oxide layer also was effective in preventing surface devitrification of the soda
lime glass surface when tin oxide was deposited at 500°C to 540°C. Thus, the aluminum oxide
is believed to act in protecting the soda lime glass surface from crystallizing around the nuclei
20 provided by the tin oxide crystals and, consequently, serving to avoid any hazing of the glass   20
during the coating process.

Example 3

A double glazed window is constructed of clear, soda-lime type glass. The glass is treated with
25 silica-type coating to eliminate haze according to the conventional procedure disclosed in U.S.   25
Patent 2,617,745.

The structure of the double glazed window is similar to that shown in Fig. 4. Interior surface
A carries 0.26-micron coating of tin oxide. Interior surface B carries a coating of 0.33 ± .02
micron coating of a tin oxide composition. Each of these coatings, when viewed alone, exhibits a
30 readily visible, highly colored, iridescent color which was dominantly red or green to most   30
observers. When assembled, substantially parallel to one another, as in the structure of Fig. 4,
the iridescent color is greatly muted whether viewed from the side of the double glazed structure
facing the sun or from the other side of the same structure.

35 ### Example 4   35

Experiments were carried out to prepare graded refractive index layers between glass (n of
about 1.5) and tin oxide (n of about 2.0) coatings. A graded layer of $Si_xSn_{1-x}O_2$ was utilized
with "x" gradually decreasing from 1 to zero as the layer was built upon the glass surface. The
SnO_2 layer was of about 0.3 microns thick; the underlying, graded area was about 0.3 microns
40 thick. The resulting structures exhibit markedly reduced interference coloration, compared to   40
layers of SnO_2 of the same thickness but without the graded interlayer region between glass and
the SnO_2.

The volatile sources of silicon are, in one instance, SiH_4 (from a 1% mixture in N_2 carrier gas)
and, in another instance, $(CH_3)_2SiH_2$ (from a cylinder of the pure gas). Deposition was carried
45 out at a surface temperature of 480°C. Gas concentrations were initially about 0.4% silane (or   45
alkyl-substituted silane), 10% oxygen, balance nitrogen. Then tetramethyltin $(CH_3)_4Sn$ was
gradually introduced up to a concentration of 1% over a period of about 3 minutes, while the
silane concentration was gradually decreased to zero over the same period. Then the carrier gas
for the tetramethyltin was cut off and the apparatus purged for about 5 minutes with air to
50 remove the last traces of the silane. Then a gas flow of 1% $(CH_3)_4Sn$, 3% CF_3Br, 20% O_2,   50
balance nitrogen, was passed under the surface for three minutes to deposit a layer of fluorine-
doped tin oxide about 0.4 μ thick.

The interference colors were considerably less vivid on these coatings with a graded refractive
index undercoat.
55   55
Example 5

A similar process is carried out using GeH_4 in place of SiH_4. The graded layer is formed of
$Ge_xSn_{1-x}O_2$ with "x" gradually decreasing from one to zero as the layer is build up on the glass.
Since the refractive index of pure GeO_2 is about 1.65, the graded layer still has a refractive
60 index discontinuity from that of glass (about 1.5). However, the uniformity of the deposition was   60
somewhat better than obtained with the SiH_4. Reductions in visibility of iridescence were noted
similar to those noted with respect to Example 4.

Examples 6-9
65 Example 1 is repeated utilizing, as the intermediate layer between glass and tin oxide, the   65

following materials selected from Table A:
Example 6: 82% In_2O_3/18% SiO_2
Example 7: 58% GeO_2/42% ZnO
Example 8: 70% Ga_2O_3/30% Al_2O_3-l
5 Example 9: 60% Al_2O_3-l/40% ZnO
Low iridescence is realized in each of these cases.

Examples 10-14
The following materials, all selected from Table B and C, are used as the two intermediate
10 layers replacing the single intermediate layers of Example 1 and 6-9:

	N of about 1.63	*N of about 1.86*
Example 10:	97% Al_2O_3-l/3% SiO_2	84% Si_3N_4/16% SiO_2
Example 11:	60% ZnO/40% SiO_2	90% ZnO/10% SiO_2
15 Example 12:	63% In_2O_3/37% SiO_2	60% SnO_2/40% Al_2O_3-h
Example 13:	70% Ga_2O_3/29% SiO_2	76% SnO/24% GeO_2
Example 14:	62% SnO_2/38% SiO_2	61% In_2O_3/39% Al_2O_3-h

Example 15
20 A tin oxide coating is placed on a glass substrate at different thicknesses. (The glass substrate 20
is first coated with an ultra-thin film of silicon oxynitride to provide an amorphous, haze-
inhibiting surface.)

Thickness of Tin Oxide	*Iridescence Visibility*
25 0.3	strong
0.6	distinct, but weaker
0.9	barely detectable except in fluorescent light
1.3	weak, even in fluorescent
30	light

The latter two materials are not aesthetically objectionable for architectural use.

A Method of Confirming Coating Quality
35 A simple method for quickly checking the refractive index of thin films was developed, in 35
order to be able to find deposition conditions for films of the desired refractive index. Suppose,
for example, a film with refractive index n = 1.74 is desired for an undercoat layer. A liquid with
this refractive index is selected. For this example, diiodomethane, n = 1.74, is used. A film
whose thickness is about 0.2 to 2 microns, is deposited on a glass surface. The coated glass is
40 observed by reflected light from a monochromatic light source, such as a filtered mercury lamp 40
at λ = 5461Å. The coated glass shows an interference pattern of dark and bright bands, if the
thickness of the film varies over the glass surface. A drop of the liquid with known refractive
index is placed on the film. If the refractive index of the film exactly matches that of the liquid,
then the interference pattern disappears under the drop.
45 If the refractive indices of film and drop do not match exactly, then the interference pattern is 45
still visible under the drop, but is weaker in intensity there. If this weak interference pattern
under the drop is a direct continuation of the band pattern on the rest of the film, then the
refractive index of the film is *larger* than that of the reference liquid. If, on the other hand, the
band pattern under the drop is reversed (light and dark areas reversed) from what is present
50 without the liquid drop, then the refractive index of the film is *smaller* than that of the reference 50
liquid.
By using this simple, but accurate, measurement of film refractive index, the conditions for
forming a film can be adjusted easily in a series of test runs, to match the desired value. By
choosing other reference liquids, one can adjust films to various other values. n = 1.63, used in
55 a two-layer undercoat, can be set using 1,1,2,2 tetrabromoethane as a reference liquid. 55
n = 1.86, for the other layer in a two layer undercoat design, can be adjusted to a solution of
sulfur and phosphorous in diiodomethane, described by West in *American Mineral*, Vol. 21, pg.
245 (1936). From the above it will also be apparent to those skilled in the art that the general
procedure can be used as a quality control tool in manufacture. Liquids of known refractive
60 index are also furnished by Cargille Laboratories, New Jersey. 60
It is to be realized the advantageous processes of the invention include the conservation of
heat in buildings with substantial areas of glass and also include the electrical heating of
windows, as in automobiles and airplanes, using the resistive features of the coatings of the
invention. In general, these coatings are ohmic, usually semiconductive.

CLAIMS

1. In a structure formed of at least one transparent glass sheet of the type comprising a first inorganic coating of an infra-red reflective material and of the type that is a transparent semiconductor and exhibits iridescent colors in daylight illumination, the improvement wherein
5 said first coating is arranged congruently with a second coating which forms means to substantially diminish iridescent colors of said first coating by providing at least two interfaces which form means, together with the mass of said second coating, to reflect and refract light such that the observability in daylight illumination of said iridescent colors is substantially reduced.

10 2. A structure as defined in Claim 1 wherein said second coating is between said first coating and said glass, and forms to reflect and refract light to add coherently to and thereby mute the iridescent reflection from said first coating.

3. In a structure formed of at least one transparent glass sheet of the type comprising a first inorganic coating of an infra-red reflective material and of the type that is a transparent
15 semiconductor and exhibits iridescent colors in daylight illumination, the improvement wherein said first coating is arranged congruently with a second coating which forms means to substantially diminish iridescent colors of said first coating by providing at least two interfaces which form means, together with the mass of said second coating, to reflect and refract light such that the observability in daylight illumination of said iridescent colors is substantially
20 reduced and wherein said second coating is between said first coating and said glass, and forms to reflect and refract light to add coherently to and thereby mute the iridescent reflection from said first coating and wherein said second coating has a refractive index defined as about the square root of the multiple of the refractive indices of said glass and said first coating.

4. A structure as defined in Claim 2 wherein said second coating has a thickness of about
25 1/4 wavelength of light having a vacuum wavelength of about 500 nanometers.

5. In a structure formed of at least one transparent glass sheet of the type comprising a first inorganic coating of an infra-red reflective material and of the type that is a transparent semiconductor and exhibits iridescent colors in daylight illumination, the improvement wherein said first coating is arranged congruently with a second coating which forms means to
30 substantially diminish iridescent colors of said first coating by providing at least two interfaces which form means, together with the mass of said second coating, to reflect and refract light such that the observability in daylight illumination of said iridescent colors is substantially reduced and wherein said second coating is between said first coating and said glass, and forms to reflect and refract light to add coherently to and thereby mute the iridescent reflection from
35 said first coating and wherein said second coating has a refractive index of from about 1.7 to 1.8 and is about 64 to 80 nanometers thick, and wherein said first coating has a refractive index of about 2, and said glass has a refractive index of about 1.5.

6. The structure of Claim 5 in which said second coating is formed from metal oxide, metal nitride, or a mixture thereof.
40 7. A structure as defined in Claim 6 in which the metal oxide and nitride compositions are selected from those disclosed in Table A of the Specification.

8. A structure as defined in Claim 5 wherein said second coating is principally formed of aluminum oxide.

9. A structure as defined in Claim 5 wherein said second coating is principally formed of
45 silicon oxynitride.

10. A structure as defined in Claim 1, wherein said second coating is an amorphous material and forms means to avoid haze-formation on said glass during application of said first coating.

11. A structure as defined in Claim 2 wherein said second coating is an amorphous material and forms means to avoid haze-formation on said glass during application of said first coating.
50 12. A structure as defined in Claim 1 wherein said second coating is between said first coating and said glass, said second coating forming a gradient, with respect to refractive index, between said glass and said first coating.

13. A structure as defined in Claim 12, wherein said first coating is fluorine doped stannic oxide.
55 14. A structure as defined in Claim 12, wherein said gradient is stepwise with a plurality of coating increments of different refractive indices.

15. In a structure formed of at least one transparent glass sheet of the type comprising a first inorganic coating of an infra-red reflective material and of the type that is a transparent semiconductor and exhibits iridescent colors in daylight illumination, the improvement wherein
60 said first coating is arranged congruently with a second coating which forms means to substantially diminish iridescent colors of said first coating by providing at least two interfaces which form means, together with the mass of said second coating, to reflect and refract light such that the observability in daylight illumination of said iridescent colors is substantially reduced and wherein said second coating is between said first coating and said glass, said
65 second coating forming a gradient, with respect to refractive index, between said glass and said

first coating and wherein said gradient is continuous with a gradually changing refractive index between glass and said infra-red reflective material.

16. A structure as defined in Claim 12. wherein said second coating comprises silicon oxynitride mixture of $XSiO_2(1-X)Si_3N_4$ where X changes from near unity at the glass surface to near zero at the boundary of said first coating.

17. A structure as defined in Claim 13. wherein said second coating comprises mixtures of $Si_xSn_{1-x}O_2$ or $Ge_xSn_{1-x}O_2$. where X ranges from near unity at the glass surface, to zero at the boundary of said first coating.

18. In a structure formed of at least one transparent glass sheet of the type comprising a first inorganic coating of an infra-red reflective material and of the type that is a transparent semiconductor and exhibits iridescent colors in daylight illumination. the improvement wherein said first coating is arranged congruently with a second coating which forms means to substantially diminish iridescent colors of said first coating by providing at least two interfaces which form means. together with the mass of said second coating. to reflect and refract light such that the observability in daylight illumination of said iridescent colors is substantially reduced and wherein said second coating comprises two layers including

(a) one film closer to the glass and having a refractive index approximately given by the formula

$$n_a = n_{ic} \cdot 26 \, n_{gl} \cdot 74$$

and

(b) a second film closer to said first coating and having a refractive index approximately given by the formula

$$n_b = n_{ic} \cdot 74 \, n_{gl} \cdot 26$$

wherein n_{ic} is the refractive index of said first coating and n_{gl} is the refractive index of the glass.

19. In a structure formed of at least one transparent glass sheet of the type comprising a first inorganic coating of an infra-red reflective material and of the type that is a transparent semiconductor and exhibits iridescent colors in daylight illumination. the improvement wherein said first coating is arranged congruently with a second coating which forms means to substantially diminish iridescent colors of said first coating by providing at least two interfaces which form means. together with the mass of said second coating. to reflect and refract light such that the observability in daylight illumination of said iridescent colors is substantially reduced and wherein said second coating comprises two layers including

(a) one film. closer to the glass and having a refractive index in a range of about 1.6 to 1.7;

(b) a second film closer to the first coating and having a refractive index in a range of about 1.8 to 1.9.

which values are effective for said first coating having a refractive index of about 2. and glass having a refractive index of about 1.5.

20. A structure as defined in Claim 19. wherein said second coating comprises two layers including

(a) one film closer to the glass and having a composition disclosed in Table B; and

(b) a second film closer to said first coating and having a composition disclosed in Table C of the Specification.

21. A structure as defined in Claim 1 wherein said first coating is stannic oxide.

22. A structure as defined in Claim 19. wherein said first coating is stannic oxide.

23. A structure as defined in Claim 1 wherein the glass comprises an amorphous film thereover.

24. A structure as defined in Claim 12. wherein the glass comprises an amorphous film thereover.

25. A structure as defined in Claim 18 wherein the glass comprises an amorphous film thereover.

26. The structure of Claim 22 wherein said second coating is silicon oxynitride.

27. The structure of Claim 23 wherein said amorphous film is silicon oxynitride.

28. The structure of Claim 25 wherein said amorphous film is silicon oxynitride.

29. A structure as defined in Claim 1 exhibiting a color saturation value below 13.

30. A structure as defined in Claim 1 exhibiting a color saturation value below 8.

31. A structure as defined in Claim 1 exhibiting a color saturation value below 5.

32. A structure as defined in Claim 1 wherein said first and second coatings together are less than 0.85 microns in thickness.

33. A structure as defined in Claim 1 wherein said semiconductor layer is less than 0.4 microns in thickness.

34. A structure as defined in Claim 2 wherein said semiconductor layer is less than 0.4

microns in thickness

35   A structure as defined in Claim 12 wherein said semiconductor layer is less than 0.4 microns in thickness

36   A structure as defined in Claim 18 wherein said semiconductor layer is less than 0.4
5   microns in thickness   5

37   A structure as defined in Claim 30 wherein said semiconductor layer is less than 0.4 microns in thickness

38   A structure as defined in Claim 2 wherein said structure comprises only glass sheets which are formed of clear glass or glass of light tint, said glass being free from metallic, gray or
10 bronze and other dark-toned tones capable of suppressing the visibility of iridescence.   10

39.   A structure as defined in Claim 12 wherein said structure comprises only glass sheets which are formed of clear glass or glass of light tint, said glass being free from metallic, gray or bronze and other dark-toned tones capable of suppressing the visibility of iridescence.

40.   A structure as defined in Claim 19 wherein said structure comprises only glass sheets
15 which are formed of clear glass or glass of light tint, said glass being free from metallic, gray or   15
bronze and other dark-toned tones capable of suppressing the visibility of iridescence.

41.   A structure as defined in Claim 30 wherein said structure comprises only glass sheets which are formed of clear glass or glass of light tint, said glass being free from metallic, gray or bronze and other dark-toned tones capable of suppressing the visibility of iridescence.

20 42.   A structure as defined in Claim 23 wherein said structure comprises only glass sheets   20
which are formed of clear glass or glass of light tint, said glass being free from metallic, gray or bronze and other dark-toned tones capable of suppressing the visibility of iridescence and reducing the transmittance of the structures to less than about 25%.

43.   A structure as defined in Claim 1 wherein said first coating and said second coating
25 spaced apart from one another are each formed of materials wherein one of said coatings differs   25
from the other of said coatings in thickness by about 1/4 wavelength of 500 nanometer light, such that together, said coatings form means to reflect and refract light which adds incoherently and markedly reduces the perceptible iridescence of said structure.

44.   A structure as defined in Claim 43 wherein said first and second coatings are on
30 separate glass plates mounted in a double glazed window structure.   30

45.   A structure as defined in Claim 43 wherein one said coat is about 0.26 microns thick and another of said coatings is about 0.33 microns thick, both coatings having a refractive index of about 2.

46.   In a process for coating transparent glass with a primary thin transparent coating of
35 infra-red reflecting semiconductor, the improvement comprising the step of forming on said   35
glass, before coating a primary infra-red reflecting semiconductor over said glass, an intermediate coating: said intermediate coating being formed of a metal oxide, a metal nitride, or mixtures thereof, and providing with said intermediate coating at least two interfaces which, together with the mass of said intermediate coating, form means to reflect and refract light such that the
40 detectability of iridescent colors is substantially reduced.   40

47.   A process as defined in Claim 46 wherein said intermediate coating has a refractive index defined as about the square root of the multiple of the refractive indices of said glass and said primary coating.

48.   A process as defined in Claim 46 wherein said intermediate coating has a thickness of
45 about 1/4 wavelength of light having a vacuum wavelength of about 500 nanometers.   45

49.   A process as defined in Claim 47 wherein the intermediate coating has a refractive index of about 1.7 to 1.8 and is about 64 to 80 nanometers in thickness.

50.   A process as defined in Claim 46 wherein said intermediate coating is an amorphous material, at least at its interface with said glass, and forms means to avoid haze formation on
50 said glass.   50

51.   A process as defined in Claim 46 wherein said intermediate coating is formed as a graduated composition gradually decreasing in silica from its interface with said glass to its interface with said primary thin coating.

52.   A process as defined in Claim 46 wherein said intermediate coating comprises silicon
55 oxynitride.   55

53.   A process as defined in Claim 46 wherein said intermediate coating is deposited in two layers as follows:

(a) one film, closer to the glass and having a refractive index in a range of about 1.6 to 1.7; and

60 (b) a second film closer to the primary coating and having a refractive index in a range of   60
about 1.8 to 1.9;
and wherein said glass has a refractive index of about 1.5 and said primary coating has a refractive index of about 2.0.

54.   A process as defined in Claim 46 wherein said primary semiconductor layer is less than
65 0.4 microns.   65

55   A process as defined in Claim 46 wherein semiconductor layer is less than 0.85 microns.

56.   In a process for avoiding the loss of heat from a building through transparent glassed areas of the building, while achieving an iridescence-free appearance for said areas, said process
5 comprising the step of reflecting infra-red radiation back into said building from a thin coating of   5
an infra-red-reflective semiconductor film on the surface of said glass, the improvement comprising the step of utilizing an intermediate layer of a metal nitride, metal oxide, or mixture thereof, between said glass and said thin coating to provide at least two interfaces associated with said intermediate layer; said interfaces, together with the mass of said intermediate layer
10 being utilized to achieve said iridescence-free appearance.   10

57.   In a process for electrically heating a window area while achieving an iridescence-free appearance for said window area, said process comprising the step of applying voltage across said thin coating of a semiconductor layer on said window, the improvement comprising the step of utilizing an intermediate layer of a conductive metal nitride, metal oxide, or mixture
15 thereof between said glass and said thin coating to provide at least two interfaces associated   15
with said intermediate layer; said interfaces, together with the mass of said intermediate layer, being utilized to achieve said iridescence free appearance.

58.   A structure formed of at least one transparent glass sheet of the type comprising an inorganic coating of an infra-red reflective and ohmic material wherein said inorganic coating is
20 at least 0.85 microns thick and forms means to suppress a visible iridescent appearance of said   20
coating which is apparent at coatings of said ohmic material at thicknesses substantially below 0.85 microns.

59.   A process for coating transparent glass with a primary thin transparent coating of infra-red reflecting semiconductor, substantially as hereinbefore described.

25 60.   A structure formed of at least one transparent glass sheet of the type comprising a first   25
inorganic coating of an infra-red reflective material and of the type that is a transparent semiconductor and exhibits iridescent colours in daylight illumination, substantially as hereinbefore described with reference to the accompanying drawings.